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CONVERSION OF NATURAL GAS TO LIQUID FUELS

V.H. Allinger

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CONVERSION OF NATURAL GAS TO LIQUID FUELS

by

V.M. Allenger*

ABSTRACT

A brief review of existing technology for the conversion of natural gas to liquids is presented. A large incentive exists to carry out this conversion in one step to improve thermal efficiency and to reduce initial capital equipment investment. Pyrolysis studies have been carried out in a tubular flow reactor of high purity alumina. Direct thermal decomposition of methane produced low liquid yields (0.02 g/L CH₄) at relatively high temperatures (900-1000°C).

Recommendations are made for reactor design in which catalytic studies on high-temperature methane conversion are to be carried out.

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LA CONVERSION DU GAZ NATUREL EN HYDROCARBURES LIQUIDES

par

V.M. Allenger*

RESUME

On présente un résumé des procédés qui existent pour convertir le gaz naturel en hydrocarbures liquides. Un procédé qui effectuerait cette conversion en une seule étape est particulièrement intéressant puisqu'il améliorerait l'économie thermique et réduirait substantiellement l'investissement initial. Des études sur la pyrolyse du méthane ont été effectuées dans un réacteur tubulaire d'alumine. La décomposition thermique du méthane à température élevée (900-1000°C) produit de faibles quantités d'hydrocarbures aromatiques (0.02 g/L CH₄).

On fait des recommandations pour la conception des réacteurs pour effectuer des expériences sur la conversion catalytique du méthane à température élevée.

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1. INTRODUCTION

The National Energy Board (NEB)'s forecasts of supply and demand of hydrocarbons (especially natural gas and crude oil) are given in Tables 1.1 and 1.2⁽²⁴⁾. Canada now has a surplus of natural gas available. Because of the lack of markets, only 71% of the available capability was used in 1980 with production averaging some 2700 PJ for the year. Additional natural gas reserves are being found and it is estimated that these frontier supplies will not be required for domestic use before 1998. On the other hand, the supply and demand for conventional crude oil is similarly imbalanced. Neither scenario presented in Tables 1.2 and 1.3 forecasts self-sufficiency. Canada will likely remain a net importer of crude oil well into the 1990's. The demand for selected petroleum products is outlined in Table 1.4. The demand for motor gasoline, the largest single oil product category in 1980, is expected to decline at approximately 1%/a. However, the demand for diesel and aviation fuels is forecast to increase at 4%/a. Given the above, it is desirable to find an economic and efficient route to convert the surplus natural gas into transportation fuels and/or chemical feedstock. This would then make Canada self-sufficient in these commodities.

Natural gas is an excellent fuel that suffers only from its bulk in the normal gaseous state. It can be compressed into heavy steel containers (CNG) or liquefied and stored in cryogenic containers (LNG), but it cannot be liquefied at room temperature, regardless of the pressure. Processes whereby natural gas (mostly methane) is converted to a more convenient liquid form for ease of transportation (especially as gasoline or diesel fuel) are of increasing interest. There are two known commercial processes which can carry out this conversion. First, the Mobil MTG process where natural gas is converted to a synthesis gas ($\text{CO} + \text{H}_2$), then to methanol and finally to high octane gasoline. Separate plants with high capital investment are then needed for the separate conversions. Second, the Fischer-Tropsch process in natural gas is also converted in the first stage to synthesis gas and then to a complex mixture of hydrocarbons from which gasoline and other products must be separated. The gasoline product is of poor quality (low RON) and the separation processes make this approach quite costly.

Table 1.1 - Supply capability of natural gas
PJ/a

	Actual 1980	Current Report	
		1985	1995
Established Reserves	3800	4139	1853
Reserves Additions	-	398	1300
Total	3800	4537	3153

Table 1.2 - Supply/Demand Balance for Crude Oil ($10^3 \text{ m}^3/\text{d}$) (Pessimistic)

	1980	1990	2000
Production	245	179	123
Requirements	300	271	306
Net imports	55	92	183
Exports	15	3	0
Total imports	70	95	183

Table 1.3 - Supply/Demand Balance for Crude Oil ($10^3 \text{ m}^3/\text{d}$) (Optimistic)

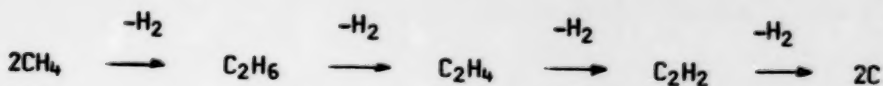
	1980	1990	2000
Production	245	230	282
Requirements	300	272	306
Net imports	55	42	24
Exports	15	4	0
Total imports	70	46	24

Table 1.4 - Demand for Selected Petroleum Products

PJ			
	1980	1990	2000
Motor gasoline	1341	1212	1115
Aviation fuels	175	235	332
Light fuel oil & kerosene	607	315	216
Diesel	581	873	1214
Heavy fuel oil	626	261	227
Petrochemical feedstock	<u>156</u>	<u>221</u>	<u>389</u>
Total	4008	3691	4178



Therefore, sufficient incentive exists to search for a more direct route for converting natural gas to liquid fuels, (e.g., gasoline, diesel). The pyrolysis of natural gas has been studied for many years and a significant amount of work has been carried out in the USSR (^{15, 37}). The pyrolysis of methane is believed to follow a stepwise dehydrogenation sequence (¹⁹):



Indeed, for many years, acetylene has been made by the homogeneous thermal decomposition of natural gas at 1500-1700°C (¹⁷). Recently, it was shown that the reactor surface can catalyze the decomposition of methane at low reaction conversions and increase the yields of the intermediate products, e.g., ethane, ethylene by as much as 300% (¹³). Rapid quenching of these products and an appropriate catalytic surface can yield benzene and higher hydrocarbons.

The objective of this project is to investigate the feasibility of producing gasoline and other hydrocarbons from catalytic pyrolysis of natural gas. The following steps are involved in the proposed research and development:

1. A literature search on existing knowledge of natural gas pyrolysis (both homogeneous and heterogeneous).
2. Design and construction of a suitable flow apparatus for flow catalysis studies at elevated temperatures.
3. Provision for analysis of gaseous and/or liquid products from reactor exit stream.
4. Screening of possible catalysts for direct conversion of natural gas to liquids.
5. Evaluation of selected catalysts in terms of performance and comparison of their chemical properties, selectivities and coking characteristics.

2. INDIRECT PROCESSES FOR CONVERTING NATURAL GAS TO LIQUIDS

2.1 Mobil Oil Process

There are three stages in converting natural gas to gasoline by the Mobil process: steam reforming, methanol synthesis and gasoline synthesis. Each is discussed briefly.

2.1.1 Steam Reforming

In the first stage of the Mobil process, methane is steam reformed over a supported nickel catalyst at 850-900°C and at a pressure of 1.6-2.5 MPa (ca 25 atm) in tubular furnaces that generally are heated with natural gas. The reaction takes place according to ⁽²⁸⁾:



with small contribution from:



When the synthesis gas produced by the reforming is destined for methanol production, a source of CO₂ is added to the reactor to use up some of the excess hydrogen efficiently via:



Table 2.1 lists typical operating conditions for a primary reformer. Sulphur is the most severe poison for catalysts for tubular steam reforming. With a good desulphurization system sulphur can be reduced to 0.05 ppm.

The reforming furnace comprises a number of tubular reactors (108 mm OD x 72 mm ID) containing the nickel catalyst arranged in a radiant heater which is the furnace proper. Hot combustion gases from the radiant section of the furnace pass around the tubular reactors and then through the convection section comprising the waste-heat boiler and other coils. This convection section is usually designed to recover as much as 90% of the total heat energy in the fuel (usually natural gas) burned in the reforming furnace and produces superheated steam at pressures above 600 psig which is used in the steam turbine which drives the centrifugal compressor for the synthesis gas⁽²²⁾.

Typical synthesis gas composition (dry basis) at the reactor exit is given in Table 2.2. Up to 95% conversion of CH₄ can be achieved in the reformer.

Table 2.1 - Natural gas reforming

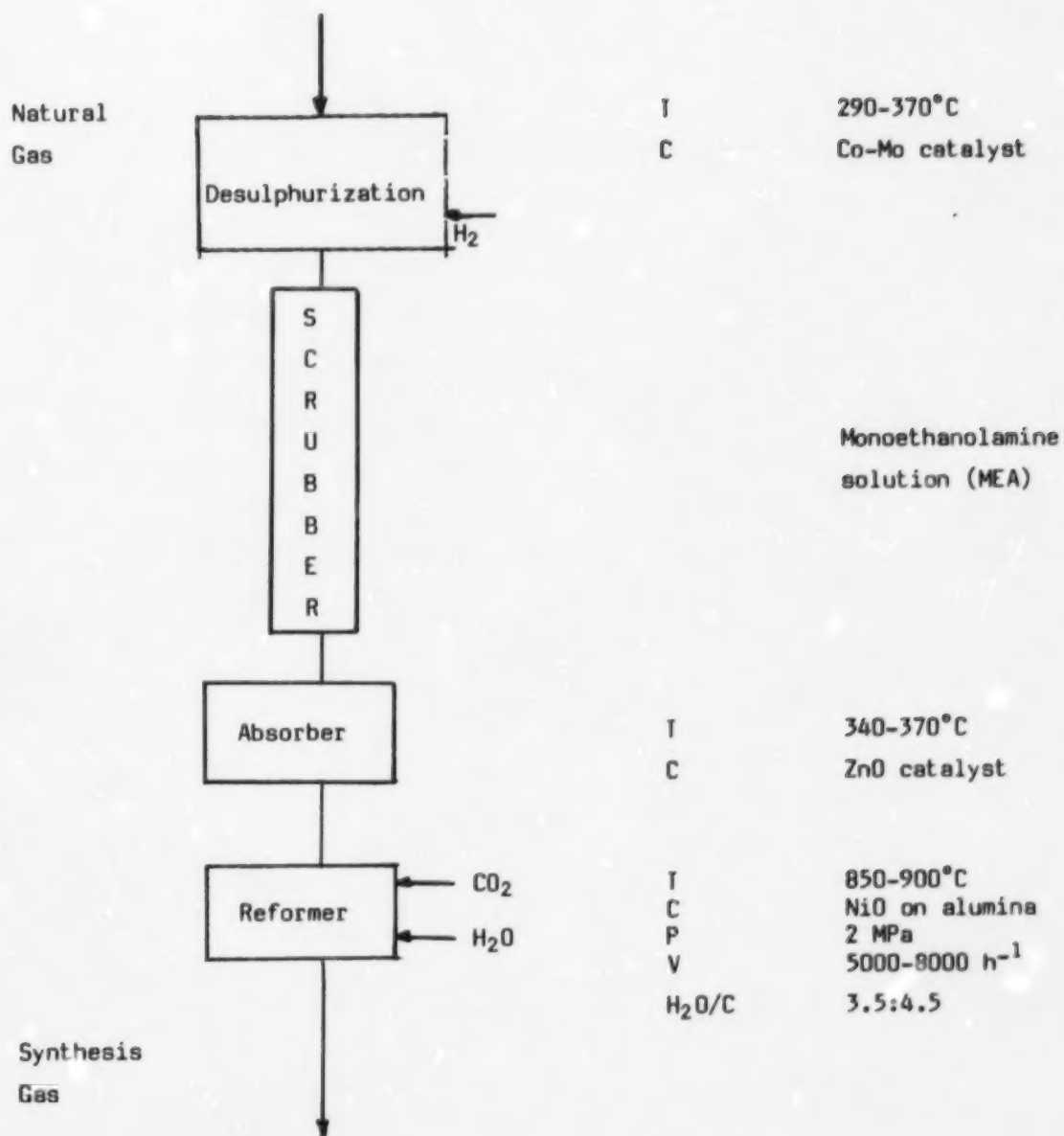
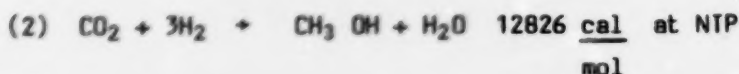
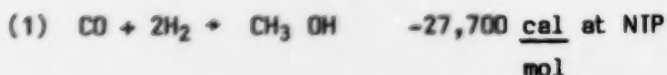


Table 2.2 - Typical composition of steam reformed natural gas with and without CO₂ added to the feed gas entering the reformer (Vol % dry basis)

	Case 1 No CO ₂ Added	Case 2 CO ₂ Added
H ₂	75.5	68.55
CO	5.74	23.15
CO ₂	14.95	5.00
CH ₄	4.65	3.20
Ar	0.03	0.20
N ₂	<u>0.13</u>	<u>-</u>
Total	100.00	100.00

2.1.2 Methanol Synthesis

In the production of synthetic methanol, synthesis gas from the reformer is often enriched with CO_2 . Since the optimum ratio of C-H is 1-2 for the hydrocarbon feed and natural gas is mostly CH_4 with a 1-4 ratio, CO_2 is added to take care of the surplus of hydrogen. Conversion of the synthesis gas to methanol takes place via the following reactions⁽²²⁾.



Several undesirable side reactions can also occur, for example:

- (1) $\text{CO} + \text{H}_2 \rightarrow \text{HCHO}$
- (2) $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$
- (3) $2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$
- (4) $2\text{CO} + \text{CO}_2 \rightarrow \text{C(s)}$

Methanol formation is favoured by low temperatures and high pressures. Catalysts for methanol synthesis are chosen for their selectivity and high activity under operating conditions. There are two proven methanol synthesis processes the Lurgi high-pressure process and the ICI low-pressure process. The traditional conversion to methanol proceeds under the high pressure of 300-350 atm in the presence of a chromium oxide-zinc oxide catalyst at about 340-400°C. This high-pressure process is shown in Fig.2.1. It requires both centrifugal (for low-pressure stages) and reciprocating piston-type compressors (for high-pressure stages) because of the low efficiency of the former at moderate plant capacities. The reaction is strongly exothermic so that provision must be made to carry this heat away. For this reason, the recycle gas for the high-pressure process contains a large amount of excess hydrogen and when combined with the feed gas the $\text{H}_2/(2\text{CO} + 3\text{CO}_2)$ ratio is often above 2.

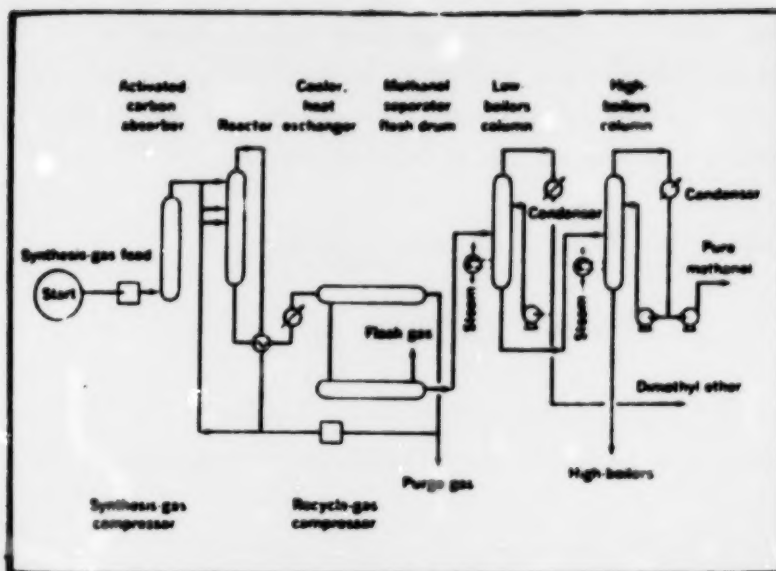
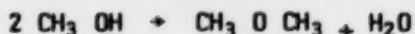


Figure 2.1- Lurgi high-pressure methanol process^a

The new low-pressure ICI process, shown in Fig. 2.2, operates at about 50 atm and 260°C and uses an active copper catalyst. The low pressures allow the use of centrifugal compressors only. It is also possible using the new catalyst to operate on hydrogen-rich synthesis gas without having to add CO₂ so as to take advantage of the mass action effect of the extra hydrogen on the equilibrium to favour methanol production. The copper catalyst has proven to have high activity and long life when using a low-sulphur feed and temperatures below 300°C. No excess hydrogen is needed for cooling purposes in the recycle loop. The lower operating temperature produces less impurities in the crude methanol. Typical operating conditions are given in Table 2.3. The steam reforming, and ICI low-pressure process can be easily integrated into a methanol and hydrogen producing plant which would result in some cost-cutting efforts as discussed in a recent article⁽²⁵⁾. The low pressure ICI process has been used in almost all of the methanol plants constructed in the past 15 years. The efficiency is estimated at 70% based on carbon atoms.

2.1.3 Gasoline Synthesis

The last link in the natural gas to gasoline process is the catalytic conversion of methanol to gasoline by using a crystalline aluminosilicate type ZSM-5 catalyst (MOBIL). Methanol is converted to dimethyl ether according to:



and then to a mixture of light olefins by dehydration. The light olefins react to form heavier olefins which then yield the desired mixture of paraffins, cycloparaffins, aromatics and remaining olefins. The remaining light olefins are then alkylated. A considerable fraction of the outflow must be recycled through the catalyst for heat removal. Catalyst regeneration is also necessary because coke formation deactivates the catalyst.

Methanol conversion into hydrocarbons takes place at 371°C and atmospheric pressure (LHSV = 0.82 h⁻¹). The conversion is highly exothermic (750 Btu/lb methanol) and heat removal from the reactor is a problem. The ZSM-5 catalyst has straight and angled channels with openings of about 6 Å⁰ and has shown high selectivity for C₅ - C₁₀ hydrocarbons. The gasoline produced has a high octane and is nitrogen and sulphur-free. The process (MTG) is believed to be over 90% efficient.

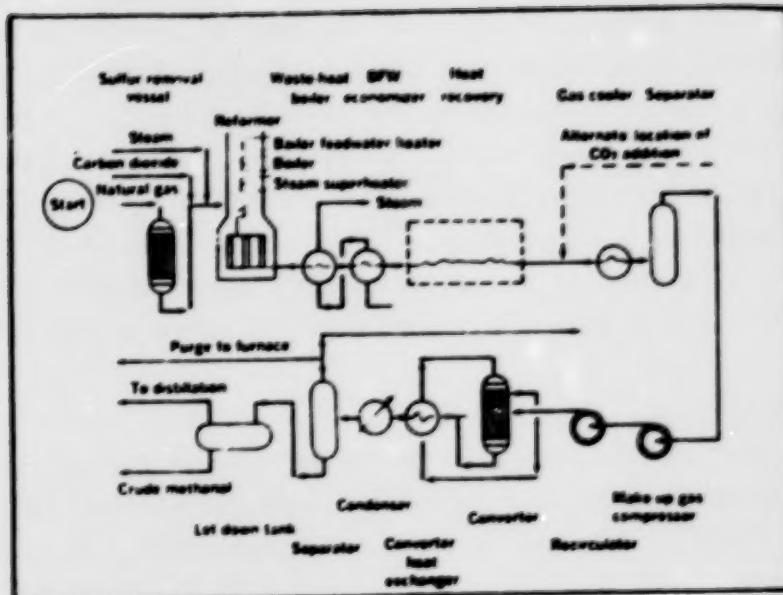
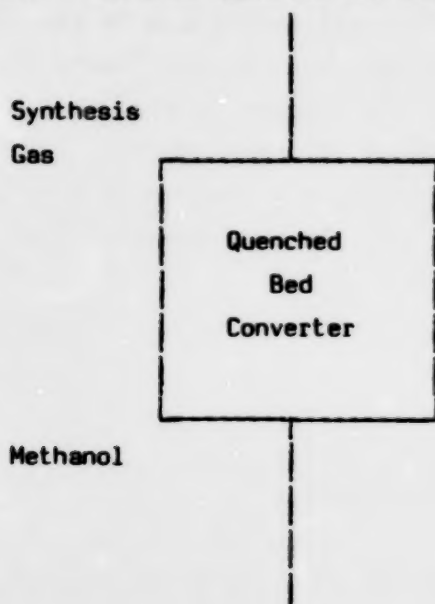


Figure 2.2- ICI low pressure methanol process

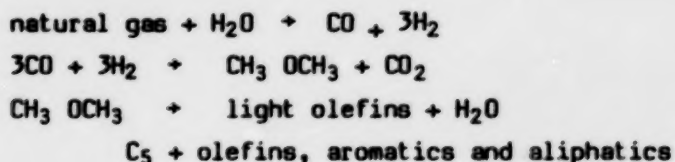
Table 2.3 - Methanol quenched bed converter operating conditions



T	=	300°C
P	=	50 atm
H ₂ :CO	=	2.3:1
GHSV	=	9000-11 000 h ⁻¹
Catalyst		Copper Based

A 12 500 bbl/d plant for converting natural gas to gasoline using a fixed bed is expected to start up in New Zealand in late 1985. A smaller pilot plant scale operation (100 bbl/day) using a fluidized bed is now being tested in West Germany.

Direct conversion of synthesis gas to gasoline can also be achieved by a continuous two-stage system where synthesis gas in an initial reactor is converted to methyl ether and then passed to the zeolite reactor where the methyl ether is converted directly to a mixture of aromatics and aliphatics⁽²⁷⁾. Methyl ether formation is achieved by passing CO/H₂ (0.25 mol ratio) over CuO and Al₂O₃ (1:1) at 316°C and 50 atm pressure. The reaction sequence is summarized as follows:



The methanol to gasoline process would add less than 15% to the investment cost of NGIG sequence. The major costs of any complete NGIG facility are in the steam reforming and conversion of syngas to methanol. "A complete plant to supply only 1% of the nation's gasoline requirements would cost several billion dollars⁽²¹⁾." ---- a significant investment. Inasmuch as the last stage in the Mobil process is very efficient (92-93%) the overall NGIG sequence efficiency is estimated at 50%.

2.2 Fischer-Tropsch Synthesis

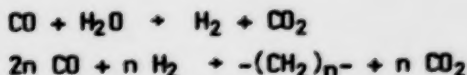
There are, in general, four stages to the natural gas to liquid products Fischer-Tropsch process as outlined below:

1. manufacture of synthesis gas
2. synthesis of hydrocarbons
3. condensation of liquid products and recovery of gasoline from product gas
4. fractionation of synthetic products

The preparation of the synthesis gas proceeds via the same route described in Section 2.1 on the steam reforming of natural gas. This synthesis gas, which consists mainly of carbon monoxide and hydrogen, is then reacted in the presence of an iron catalyst at 200-350°C and 20-2500 kPa. The main reaction can be summarized by:



In the presence of an iron catalyst, this reaction is followed by the water-gas shift reaction:



The conversion is strongly exothermic (1×10^4 kJ/kg of hydrocarbon). The water-gas shift reaction reduces the hydrogen demand so that the use of synthesis gas with a low hydrogen content is possible. Although only the iron catalyst is currently of technical importance, cobalt and nickel have also been successful on a small scale.

The heart of the Fischer-Tropsch process is the hydrocarbon synthesis reactor. The reactor and its operating conditions determine the product distribution and the upgrading scheme. Two reactor designs have been commercially proven: the Arge fixed bed and the Synthol entrained bed reactors. Sasol has been operating these two types of reactors in South Africa for over thirty years. Table 2.4 lists the typical product distribution from the respective reactors^(8,30).

The Arge reactor consists of 2052 tubes (12 m long by 0.46 m diameter) which are filled with 40 m³ of granular iron catalyst. Operating conditions are 210-250°C and 25-2500 kPa (H₂/CO:1.8). Uniform loading of the catalyst presents some problems. Because of the strong exothermic reaction the tubes are cooled by water boiling under pressure. However, this is usually insufficient heat removal. The maximum Arge synthesis gas conversion is 50% (quite low) under typical conditions.

Table 2.4 - Fischer-Tropsch process product distribution

		Fixed Bed Arge	Entrained Bed Synthol
CH ₄		2.0	10
C ₂ H ₄		0.1	4
C ₂ H ₆		1.8	4
C ₃ H ₆		2.7	12
C ₃ H ₈		1.7	2
C ₄ H ₈		2.8	9
C ₄ H ₁₀		1.7	2
C ₅ -C ₁₁	Petrol	18.0	40
C ₁₂ -C ₁₈	Diesel	14.0	7
C ₁₉ -C ₂₃	Heavy Oil	7.0	-
C ₂₄ -C ₃₅		20.0	4
C ₃₅ +	Wax	25.0	-
Oxygenates		3.2	6

The Synthol reactor is 40 m high x by 2.5 m diameter. The iron catalyst is a powder made from mill scale. The recirculation rate is 8000 tons/hr and the mean catalyst life is 42 d. Operating conditions are 300-340°C and 2300 kPa ($H_2/CO:6$). Two cooling elements are installed in the reaction zone with recirculating oil as the cooling medium. The gas stream and catalyst leaving the reactor are separated in a settling chamber and the hot catalyst is returned to the reactor through a lift pipe.

Other processes such as three-phase reactors were tried at the pilot scale and show considerable potential in hydrocarbon synthesis. Nevertheless, process economics and a worldwide oil glut make further developments unwarranted.

The reactor effluent is cooled, whereby hydrocarbon products and the reaction water are condensed. A portion of the residual gas is mixed with fresh synthesis gas and after heat exchange returned to the reactor. The remainder of the tail gas is cooled stepwise to low temperature to recover light products. Sasol-type units have about a 60% overall thermal efficiency(8).

Tables 2.5 and 2.6 list some characteristic data for motor fuels from the Arge reactor. The main products of the Fischer-Tropsch process are unbranched paraffins and olefins. Gasoline made by the Arge process is very low in octane number. Synthol gasoline on the other hand has a higher octane number, however the cetane number of the diesel oil is lower.

3. DIRECT CONVERSION OF NATURAL GAS TO LIQUIDS

3.1 Thermodynamic Feasibility

From the free-energy change of a proposed reaction, predictions may be made as to its possibility and the conditions of temperature and pressure required. To examine the feasibility of direct production of higher hydrocarbons from methane, which is the major constituent of natural gas, data on the standard free energy of formation, standard enthalpy of formation and specific-heat as a function of temperature are necessary. Specific-heat data for hydrocarbons at relatively high temperature are not readily available, and extrapolations of existing specific heat correlations must be made⁽³³⁾.

Table 2.5 - Characteristic data for motor fuels from Arge synthesis

	Gasoline	Diesel oil
Specific Gravity	0.71 - 0.72	0.79 - 0.81
Aromatics (wt%)	10 - 20	10
Naphthenes (wt%)	-	5
Research Octane No.	95	-
Cetane No.	-	70

Table 2.6 - Motor fuels from Fischer-Tropsch synthesis

	Fixed bed		Entrained bed	
	Gasoline	Diesel	Gasoline	Diesel
Olefins	50	40	70	60
Paraffins	45	55	13	15
Oxygenated CPDS	5	5	12	10
Aromatics	-	-	5	15

For a reaction to be thermodynamically possible the change in the Gibbs free energy of reaction must be negative, i.e., the free energy of the products must be less than the free energy of the reactants. If this condition does not exist then the reaction cannot be induced to proceed even by means of a catalyst. Fig. 3.1 shows the free energy of formation per carbon atom for several hydrocarbons as a function of temperature. Details of the derived values and corresponding calculation procedures are given in Appendix A. Several points will be noted in this figure. At any given temperature the tendency of a reaction is from a higher curve to a lower curve ($\Delta G_f < 0$). Acetylene is the only hydrocarbon whose stability is increased with temperature, however it never becomes stable with respect to its elements C and H_2 .

The condensation of methane to higher paraffin hydrocarbons such as hexane and heptane is not possible thermodynamically. However, small amounts of ethylene, acetylene, propylene and benzene seem to be possible equilibrium products at higher temperatures although the largest driving force remains to the elements.

Furthermore, from Fig. 3.1, it can be seen that methane is very stable compared with other hydrocarbons at temperatures as high as 1200°C . Because of this, methane requires high temperatures for chemical dissociation. The thermal decomposition of methane at high temperatures consists of a series of consecutive reactions which are of primary, secondary, tertiary, etc., nature. The primary products of decomposition are in no way connected with real equilibrium. Therefore, the primary products are not stable under the reaction conditions and they decompose to secondary, tertiary compounds, etc. The final products of every pyrolysis of methane tend towards carbon and hydrogen. Only small quantities of simple hydrocarbons such as methane, ethylene and acetylene can exist in the system of hydrogen and carbon at $1200\text{--}2000^\circ\text{C}$ when true equilibrium is established.

Happel and Kramer have presented a set of calculations (by Duff and Bauer) to determine the equilibrium mole fractions in the carbon-hydrogen system at elevated temperatures ($500\text{--}5000\text{K}$) and total pressures ($0.1\text{--}10\text{ atm}$)⁽¹⁷⁾. Two basic cases were treated by these authors. The first set of results was obtained under the assumption, at a particular temperature and pressure, that equilibrium was attained for various C-H species under the

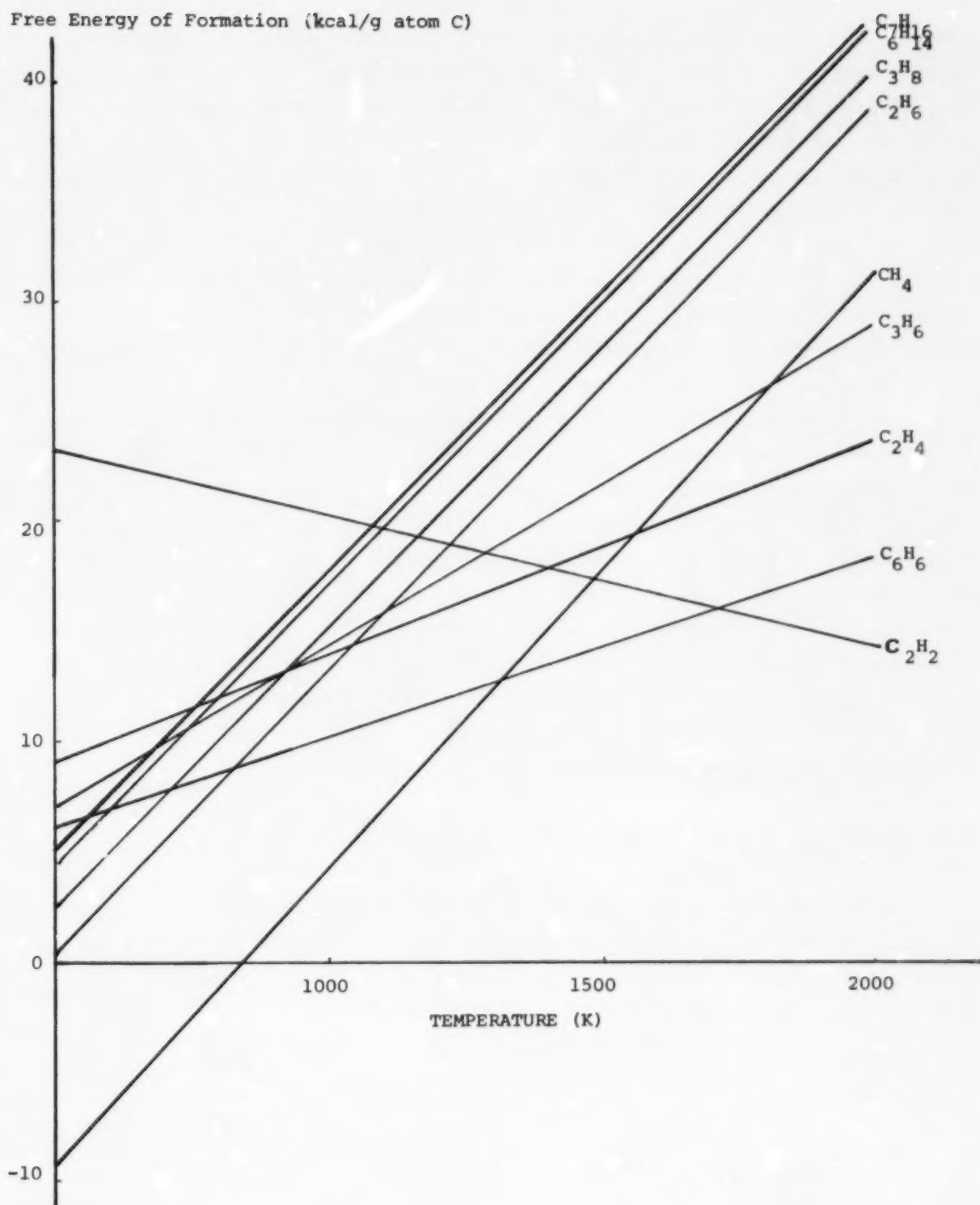


Figure 3.1 Free Energy of Formation of some Hydrocarbons

restriction that no solid carbon was allowed to precipitate. The second set of computations was performed under the assumption of complete equilibrium including the presence of solid carbon. Fig. 3.2 is a plot of temperature versus equilibrium partial pressure abstracted from Happel and Kramer's publication. It shows the most abundant species present at C/H atomic ratio of 1:4 (corresponding to methane) and at a total pressure of 0.1 atm. As can be seen, benzene, ethylene and acetylene have significant equilibrium yields at $T > 1700^\circ\text{C}$. Calculations allowing for equilibrium with solid carbon show that the vapour phase is substantially H_2 from 1000-3000 K. At temperatures up to 3000K almost all of the gas phase consists of CH_4 , H, H_2 . Further, ethylene does not attain as high values when C solid is present.

The equilibrium composition points to those species which are present in appreciable concentrations and suggest that they may be most important to the kinetic processes which lead to equilibrium. Happel and Kramer postulate that with naturally occurring hydrocarbons (including methane) which are rich in hydrogen, the first pass through the rapid heating and quenching cycle should lead to products which are carbon rich (C_2H_2 , C_6H_6 , etc.) and hydrogen⁽¹⁷⁾. Whether such a process would be useful depends on the possibility of finding experimental conditions which permit the attainment of a pseudoequilibrium state and subsequent quenching without excessive precipitation of carbon.

3.2 Previous findings of methane pyrolysis

3.2.1 Elementary thermal decomposition of methane

The equation $\text{CH}_4(\text{g}) \rightleftharpoons \text{C} + 2\text{H}_2(\text{g})$ expresses the methane equilibrium. Equilibrium constants for the decomposition at various temperatures can be obtained from the free energy calculations of Section 3.1 (based on graphite). Furthermore, the composition of the gas phase can be computed from the following:

$$K_p(T) = \frac{[\text{H}_2]^2 P}{[\text{CH}_4]}$$

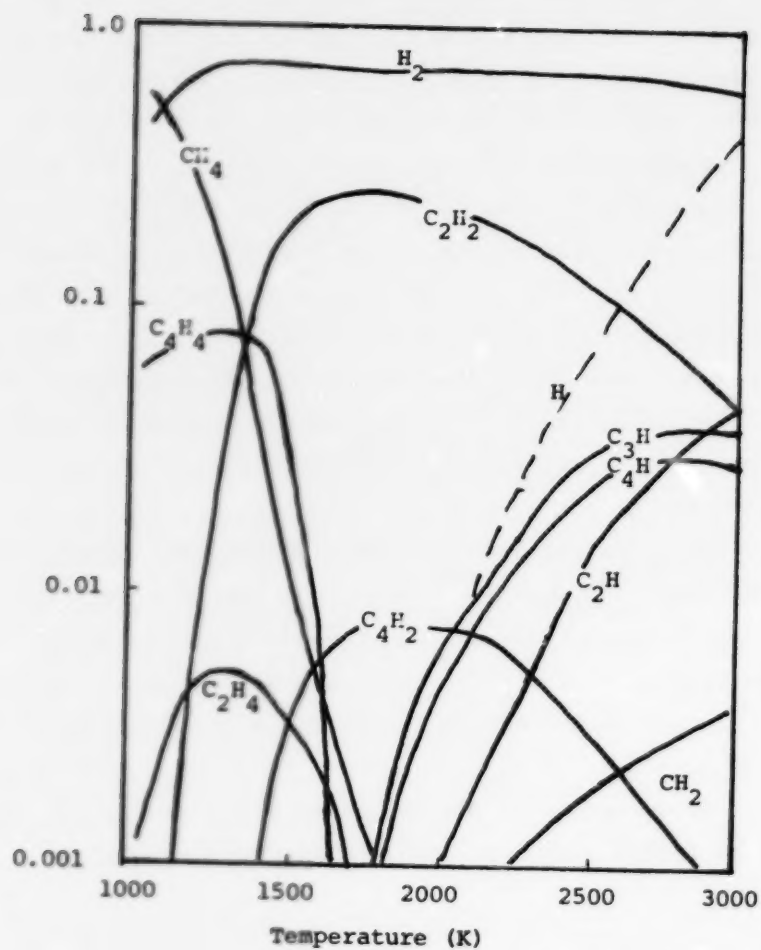


Figure 3.2 Carbon-Hydrogen Equilibrium
(no solid carbon present) ,

Pressure 0.1 atm. $C/H = 1/4$

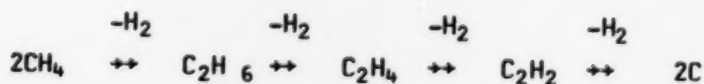
as illustrated in Fig. 3.3. For temperatures above 1500K and 101 kPa pressure the equilibrium is displaced far to the right of the reaction and the gas phase is essentially pure hydrogen. Rostrup-Nielsen has investigated the CH_4 decomposition equilibrium at 400-600°C using a thermobalance and his results are summarized in Table 3.1 and Fig. 3.4⁽²⁸⁾.

3.2.2 Kinetics of methane decomposition

Although there has been considerable interest and research on methane pyrolysis in recent years, the kinetics and mechanism are not yet fully understood. A survey of recent pyrolysis literature was made by Khan and Crynes⁽¹⁹⁾. Various techniques used in the study of methane pyrolysis include the shock tube, flow and static reactor, plasma jet, steam cracking, etc. In shock tube studies ("wall-less" reactors) it is possible to investigate reaction behaviour at considerably higher temperatures and with extremely short residence times, with no reactor surface effects⁽²³⁾. Static systems are limited to about 1100K by the time taken to admit gas to the reaction vessel and remove it at low enough conversions to study the early stages of the reaction⁽¹⁾. Flow systems, with time resolution of 10^{-1} or exceptionally 10^{-2} s extend the temperature range, and methane pyrolysis at low conversions can be explored in flow reactors at temperatures as high as 1700K.

Pyrolysis of methane at 900-1500°C yields hydrogen, ethane, ethylene, acetylene, light oil, tar and carbon. The relative amounts of the reaction products depend upon reaction conditions (especially temperature, pressure and residence time). At very high temperatures, ethane and ethylene are short-lived. At long reaction times, the acetylene formed is decomposed to carbon and hydrogen.

The mechanism of the decomposition of methane at high temperatures is believed to follow a stepwise dehydrogenation sequence as shown below:



A lower activation energy for the last step compared with the first makes it possible to obtain high yields of acetylene from methane⁽³⁴⁾. By choosing proper temperature and residence time, polymerization of intermediate products may lead to the tars and light liquids also found as reaction products.

Temperature (K)

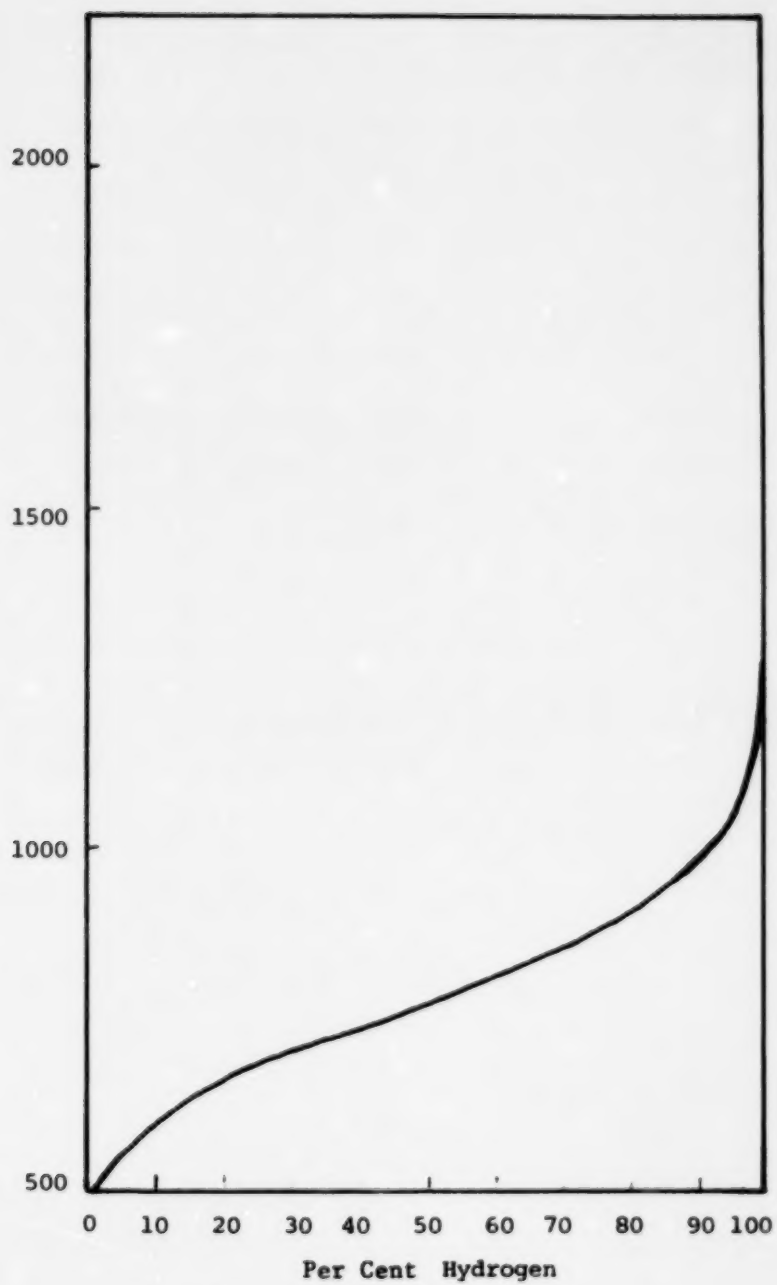


Figure 3.3 Methane Equilibrium

Table 3.1 - CH₄ decomposition - Experiments with catalyst Al

Exp. No.	Temp. °C	CH ₄ vol%		Pressure P mm Hg	K _p observed atm	K _p graphite data atm	ΔG _f kcal/mol
		Start of coke formation	Equil. comp.				
616	40	96.2	88.3	758	0.0155	0.0636	1.88
494	400	94.9	88.3	761	0.0155	0.0636	1.88
614	450	88.3	75.0	760	0.0833	0.1826	1.13
611	500	77.7	56.5	760	0.335	0.4619	0.56
617	500	77.0	58.4	762	0.296	0.4619	0.68
495	500	77.0	59.2	764	0.283	0.4169	0.75
610	550	60.0	42.8	762	0.764	1.0524	0.52
618	600	47.3	32.2	762	1.43	2.195-	0.74
496	600	41.2	31.0	772	1.38	2.195-	0.80
Dent ⁻²	410		86.0	(705) ^b	0.0055	0.0785	3.53
	423		61.8	(750) ^b	0.214	0.6968	1.80

b n₂ as balance to total pressure 760 mm Hg

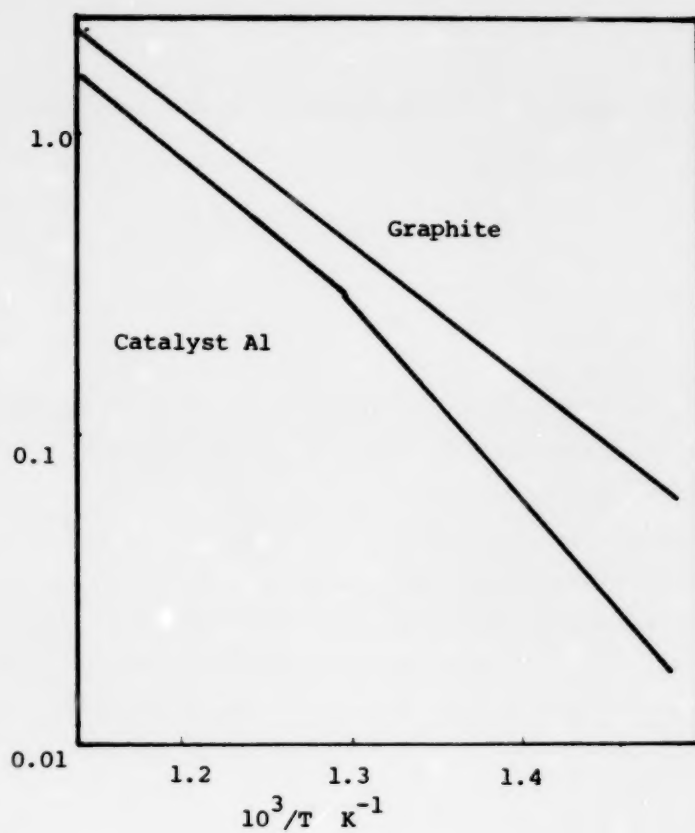
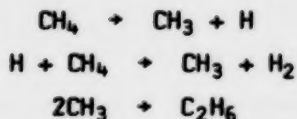
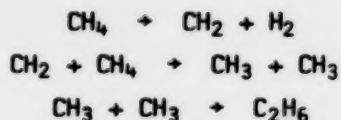


Figure 3.4 Methane decomposition on Catalyst Al

The initiation step in the proposed mechanism is believed to occur via the following sequence of reactions⁽⁴⁾:



although there still appear to be some support for the alternate route via a methylene radical⁽¹⁹⁾.



Generally, there is agreement that decomposition is a first-order reaction in methane with overall activation energies reported anywhere from 86.6 kcal to 103 kcal depending on reactor set-up.

Data reported covered a temperature range from 927-2200°C at essentially atmospheric pressure. Various diluents such as argon, hydrogen, nitrogen and helium were also used. Surface effects are also noted by some investigators. These heterogeneous effects may be related to (1) the surface composition, (2) the surface volume geometry, and (3) the presence of fine particles of carbonaceous material. This question is as yet unresolved.

3.2.3 Non-Catalytic Studies

Table 3.2 summarizes the methane pyrolysis studies in flow reactors where liquid products were obtained. Because of the severe temperatures, porcelain and quartz reaction tubes predominate. Of note however is the use of copper tube which also gives comparable liquid yields. Iron, steel and nickel however appear to promote elementary decomposition to carbon.

The light liquid product was identified as benzene by earlier workers. Toluene, xylene, ethylbenzene, etc., were also identified indicating the presence of methyl radicals. The tarry material contains largely aromatic compounds. These consisted of multiple-ring types such as naphthalene,

Table 3.2 - Summary of studies on the direct conversion of natural gas to liquids

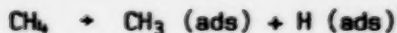
REFERENCE	TEMPERATURE [°C]	LIQUID [g/L]	TAR [g/L]	GAS (%) UNSATURATES	H ₂
Hague and Wheeler (1929)	950	-	-	4.6	31.5
Vysoky (1929)	1000	0.0253	-	-	-
Padovani (1932)	1050	0.0365	-	-	-
Boomer (1930)	1100	0.0407	-	-	-
Stanley and Nash (1929)	1150	0.0281	0.0352	3.7	32.8
Smith, Grandone and Rall (1931)	1200 1240	0.0310 -	0.04 -	- 4.4	- 39.6
Dustan, Hague and Wheeler (1934)	-	0.0351	-	-	-
Wheeler and Wood (1928)	1000	0.021	-	3.0	42.6
Present work	1000	0.02	0.01	1.0	32.3

anthracene, acenaphthene and phenanthrene with styrene as the intermediate member; all suggested a combination of the acetylene molecules by repeated coupling with ring closures⁽¹⁰⁾.

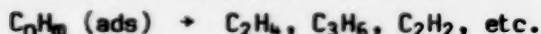
The average yield at 1000-1200°C of light liquid and tar is 0.038 g/L CH₄ and 0.034 g/L CH₄ respectively. Acetylene and ethylene (4.1%) are found to predominate as unsaturates in the product gas.

3.2.4 Catalytic Studies

The use of catalysts such as iron, nickel, cobalt, copper, platinum, palladium, and a number of refractory compounds (carbides of Cr, Mo, W, Si) has not been successful to date in increasing unsaturated compound yields, e.g., C₂H₄, C₂H₂ from the thermal decomposition of methane⁽¹⁴⁾. However, in a recent study of methane decomposition in a flow reactor, Fan and Yeh reported a positive catalytic effect on the decomposition over a thorium oxide-silica (ThO₂/SiO₂) catalyst at low conversions, as shown in Fig. 3.5^(13, 14). They contend that the following methane-metal oxide interaction takes place:



followed by:



Pyrolytic carbon was investigated by several workers and found to have deleterious effects on product yields and distribution^(1, 7).

4. EXPERIMENTAL WORK

4.1 Introduction

Renewed interest in the formation of solid, liquid and gaseous products by thermal decomposition of methane emerges from the need to better utilize large reserves of natural gas. The aim of this investigation is to explore the operating region where the decomposition reactions yield appreciable

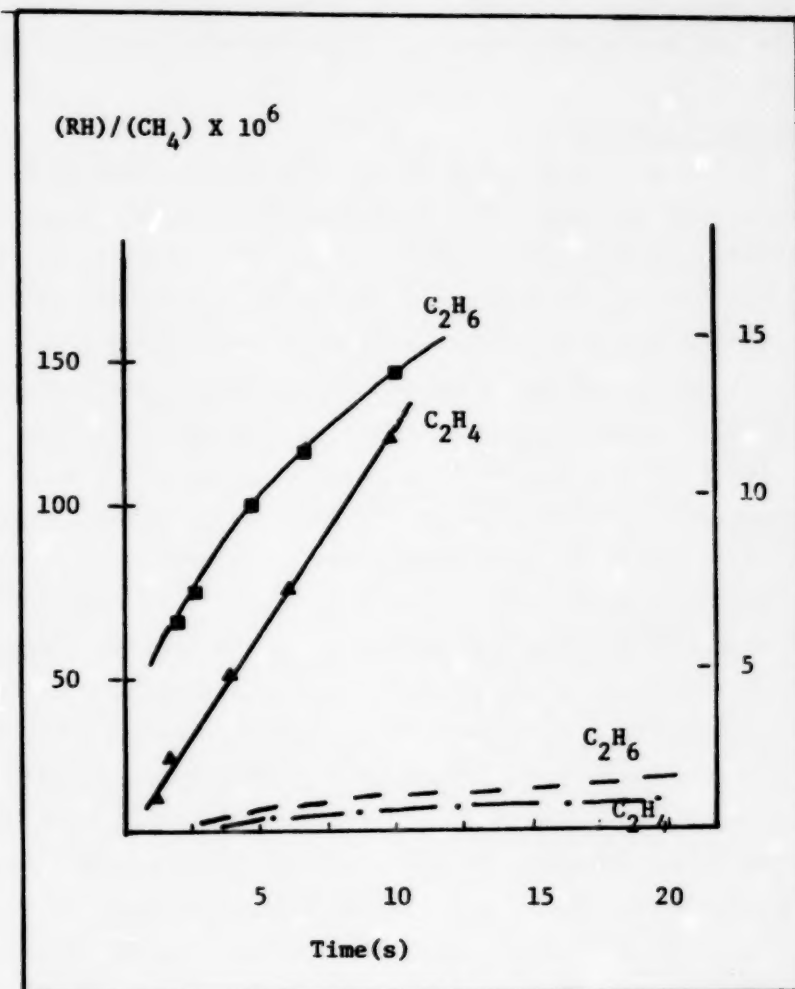


Figure 3-5 Product distribution for decomposition over ThO_2/SiO_2

products other than carbon and hydrogen. Accordingly, the homogeneous decomposition of methane was investigated in a flow reactor at atmospheric pressure. Equilibrium considerations required temperatures of 900°C and greater before appreciable amounts of liquids were produced.

4.2 Experimental system

The experimental system (Fig. 4.1) consists basically of an inlet gas manifold, a reaction tube and a product gas train. The reactor is a high purity impervious 998 Alumina tube (McDanel Ref.) 5.08 cm ID, 5.715 cm OD and 90 cm long. Heating was supplied by a Lindberg high temperature electric furnace using double-end silicon-carbide heating elements which are horizontally positioned above and below the furnace chamber. The furnace ends were very well lagged with ceramic fibre insulation capable of withstanding 1500°C. The furnace temperature was controlled by means of a Pt-Rh (13%) thermocouple which was imbedded in the insulation in the centre of the furnace. A second Pt-Rh thermocouple was inserted coaxially within the reactor with the measuring junction at the inside wall of the tube. This thermocouple averaged about 100°C below that indicated by the control thermocouple. About 5 to 6 h were necessary to achieve the required temperature as the heating rate was limited to 5°C/min to prevent thermal shock damage to the alumina. The experiments were performed at atmospheric pressure between 900-1100°C and gas flowrates of 0.5-5.5 l/min at NTP. The flow conditions were laminar as the Reynolds numbers were less than 2100. Methane and nitrogen (used to purge system) were passed from storage cylinders to float-type rotameters where flowrates were metered. Both gases were supplied by Matheson Gas Co. (99.5% purity). Methane was subsequently passed over a Radox reagent to remove traces of oxygen before entering the reactor.

From the furnace the product gases entered a glass receiver packed loosely with glass wool, a water cooled condenser followed by two traps kept at dry-ice temperature by a solution of solid carbon dioxide in butanol. The exit gas stream then passed through a wet test meter and out through a vent line. Sampling of this stream was carried out at regular intervals. After each experiment, products condensable at -78°C were removed from the traps, weighed and analyzed. The reaction tube was removed from the furnace and the carbon deposition scraped from the walls of the reactor. A small amount of soot escaped from the reactor and small amounts of soot and tar collected at its exit making quantitative determination extremely inaccurate.

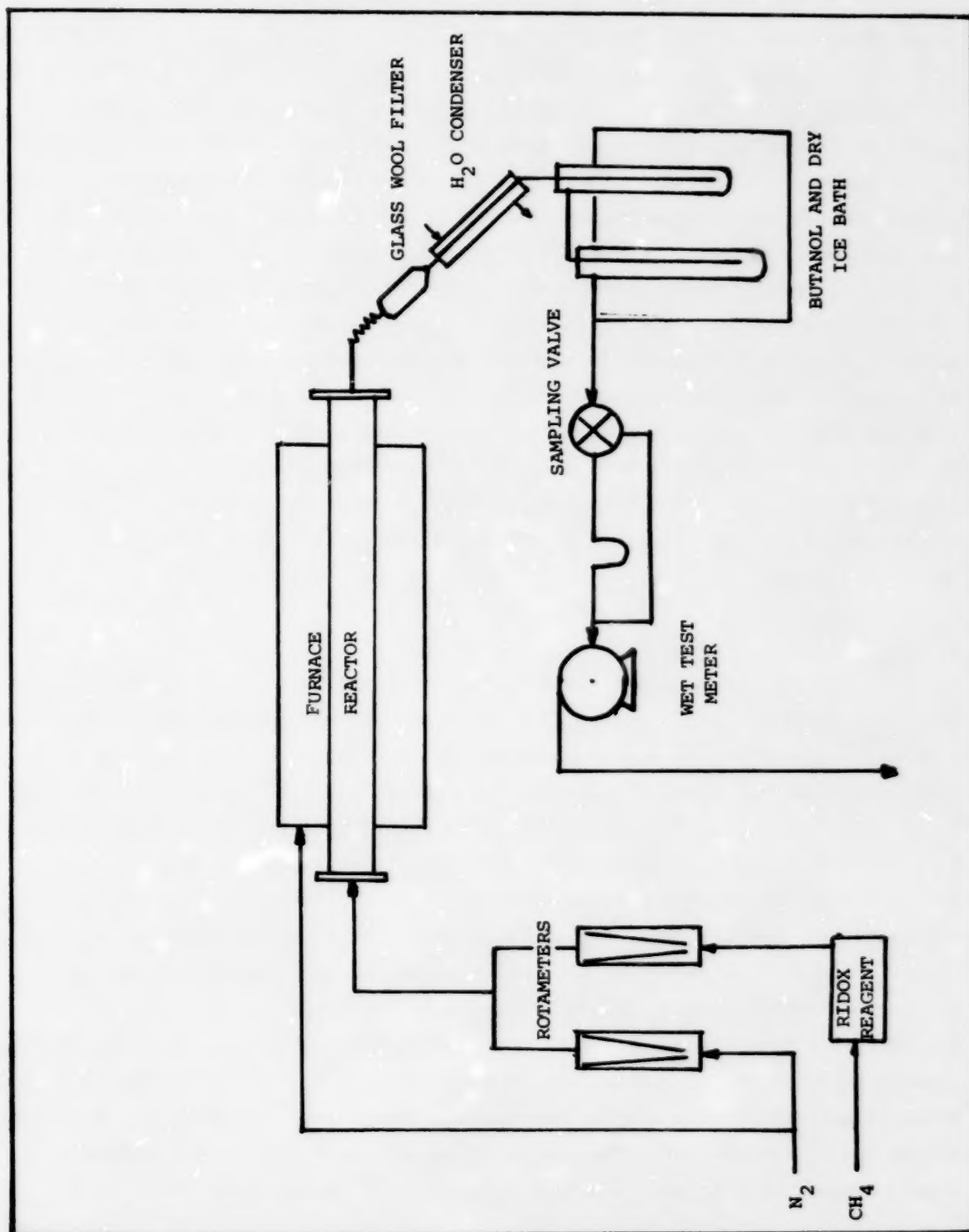


Figure 4.1 Experimental Set-up

ANALYSIS

The gaseous pyrolysis products were analyzed using a Perkin Elmer Sigma 1B Analyzer (FID). The column arrangement consisted of 11 feet of 13% DEMA + 65% DEHS on chromosorb P 80/100 mesh, 6 feet of 50% Poropak Q and 9 feet of Molecular Sieve 13X. The main products were methane, hydrogen, ethane, ethylene, propylene and other unsaturates. Analysis of the condensed liquids was obtained using a Hewlett-Packard 5880A Series Gas Chromatograph (FID) with a 20 inch, stainless steel column filled with 10% UC-W982 on Chromosorb P-Aw at a programmed temperature of 10°C/min. Analysis by GC/MS identified benzene, toluene, xylene, styrene, indene and naphthalene in the light liquid product. The tarry material adhering to the glass wool was dissolved in carbon disulphide and a GC/MS analysis showed the presence of indene, naphthalene, tetrahydroacenaphthene, acenaphthene, anthracene and flouranthenes. These products are similar to those reported in previous pyrolysis of methane studies in both static^(5,6) and flow⁽¹¹⁾ systems. Elemental analysis of the carbon deposits inside the tube indicated the presence of hydrogen in small amounts (0.44%). Approximately 8% of the carbon residue was non-combustible using an ASTM method.

4.3 Results and Discussion

A series of 10 experiments were carried out in the flow reactor described earlier. A minimum of 75 L of methane passed through the reactor. Traces of oils condensed in the cooling train at a nominal tube temperature of 900°C and these could not be measured accurately. At 1000°C, a dark fog filled the glass wool filter, tar deposited in the connections between the reaction tube and the condensers and crystals smelling strongly of naphthalene were formed. Examination of a typical simulated distillation curve (Fig. 4.7) of the pyrolysis products shows that these products cover a wide range of boiling points. The efficiency of the quenching system varied between experiments due to the changing flow rates of the reactor exit gases. Table 4.1 gives a typical gas composition as a function of time. Although the concentrations of gaseous products, e.g., ethane, ethylene and other unsaturates are accurate portrayals of their values after the quench, they do not represent these values at the end of the reactor. The distribution and yield of the -C₂- product depend dramatically on the quenching efficiency. Polymerization reactions of

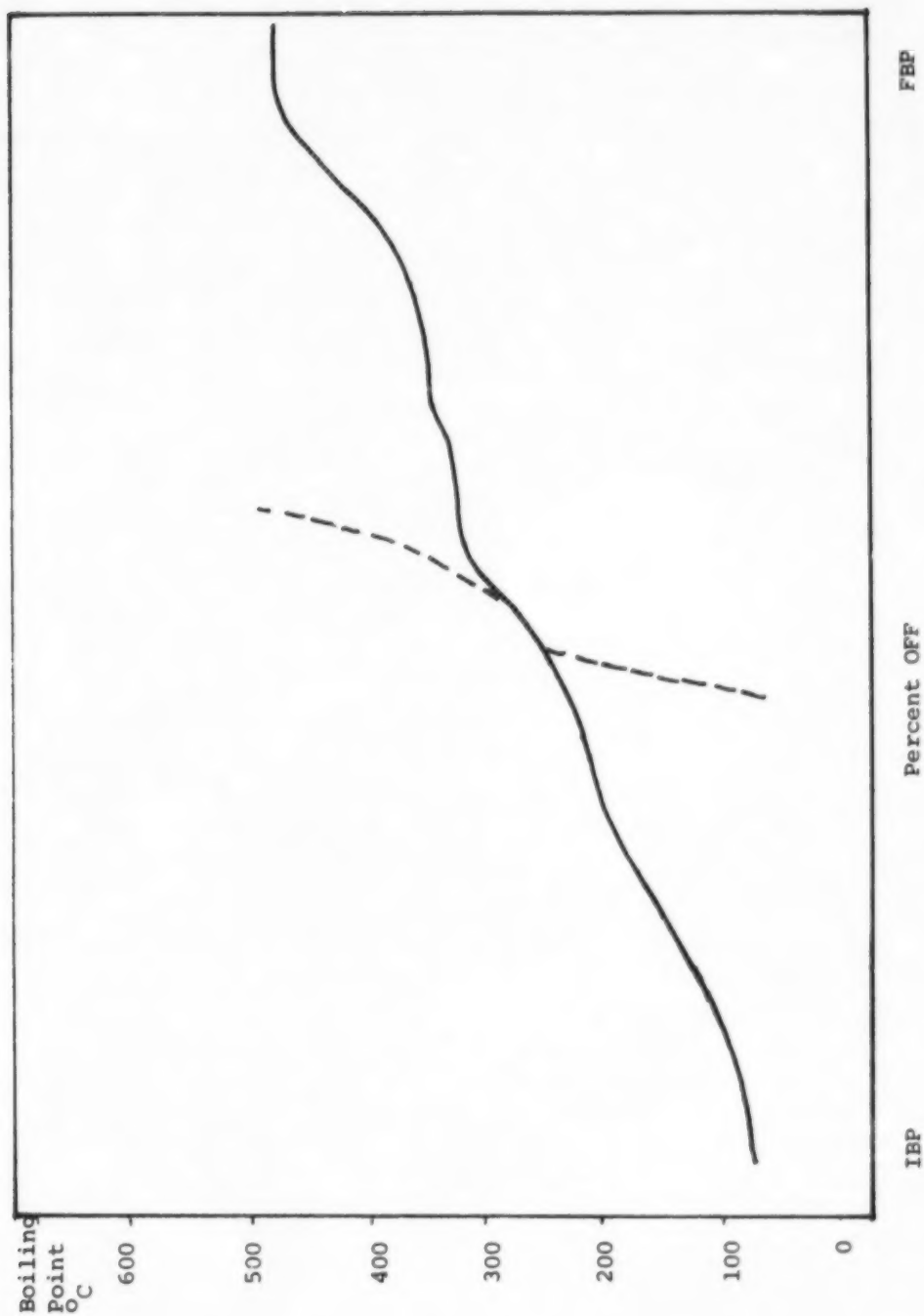


Figure 4.7 Simulated Distillation of Methane Pyrolysis Products
Temperature 1000C, Pressure 1 atm.

Table 4.1 - Gas composition as a function of time

Time [Min]	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C H ₂ n
25	28.43	69.40	1.53	0.14	0.28	-
35	29.66	69.0	0.79	0.15	0.31	-
50	30.34	68.1	0.78	0.15	0.32	0.1
65	30.09	68.87	0.41	0.17	0.31	-
80	32.23	66.79	0.29	0.18	0.29	0.11
85	32.25	66.8	0.21	0.19	0.28	0.1

the unsaturated products can continue to take place at much lower temperatures than reaction temperature. Carbon deposited within the reactor in the high heat section had two forms - one was powdered and the other had a shiny metallic appearance and was removed from the reactor tube walls in curling sheets. As suggested by Holman, two modes of carbon formation may occur⁽¹⁸⁾. Some of the carbon may be formed by dehydrogenation of methane giving a graphite-like deposit on the reactor surface. At higher conversions of methane, carbon is formed from acetylene giving a soot-like carbon in the reactor. At 1100 °C, plugging from soot-like carbon in the reactor exit and quench zone limited the experimental time to 20 min. No liquid products were obtained.

The conversion of methane (based on product gas analysis) as a function of temperature is plotted in Fig. 4.2 at a residence time of 30 s. The combined tar plus liquid yield for these experiments is shown in Fig. 4.3. It should be noted however that reaction temperature is not known accurately in these flow experiments and a flat temperature profile over more than a few centimeters of the reactor is highly unlikely.

The effect of residence time on both conversion and liquid and tar product yield is plotted in Fig. 4.4 and 4.5. Trends in these data are similar to those of previous workers. However, total liquid yields are considerably lower than reported in the literature at similar nominal temperatures. Two explanations for this are possible.

First, the yield and product distribution of the pyrolysis of methane depend on the reaction conditions (gas, temperature, reaction pressure and gas residence time). For example, liquid products have been found when pyrolysis temperatures are below 1250°C and residence times below 60 seconds at pressures of 1 atm⁽³⁶⁾. At extremely low residence times (10^{-4} - 10^{-3} s) and very high temperatures (1500-2200°C) almost complete conversion to acetylene was found^(18, 33). The interaction of these three parameters is therefore of prime interest in trying to optimize the desired product distribution. Reaction temperature and gas residence time depend largely on the overall design of the reaction system. High heat fluxes, low thermal gradients and turbulent flow conditions are requirements which must be met by any reactor system. In flow reactors, basically, clearly defined heat-up and cool-down

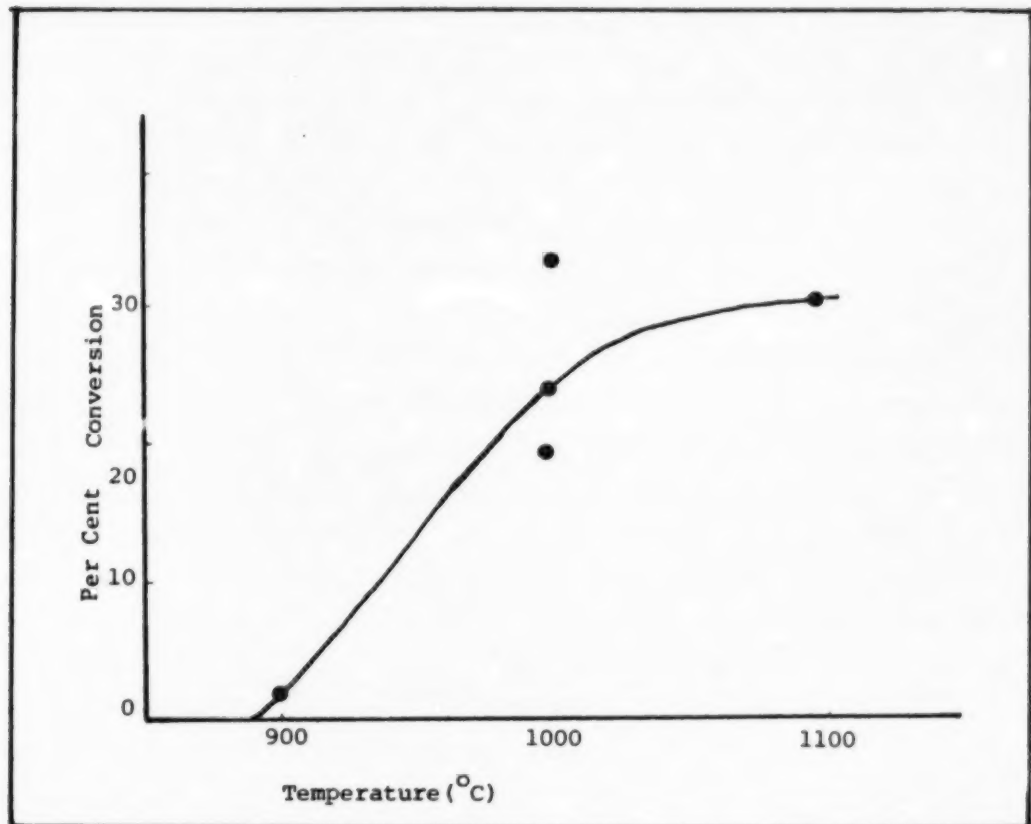


Figure 4.2 Conversion as a function of Temperature

Residence Time 30 s

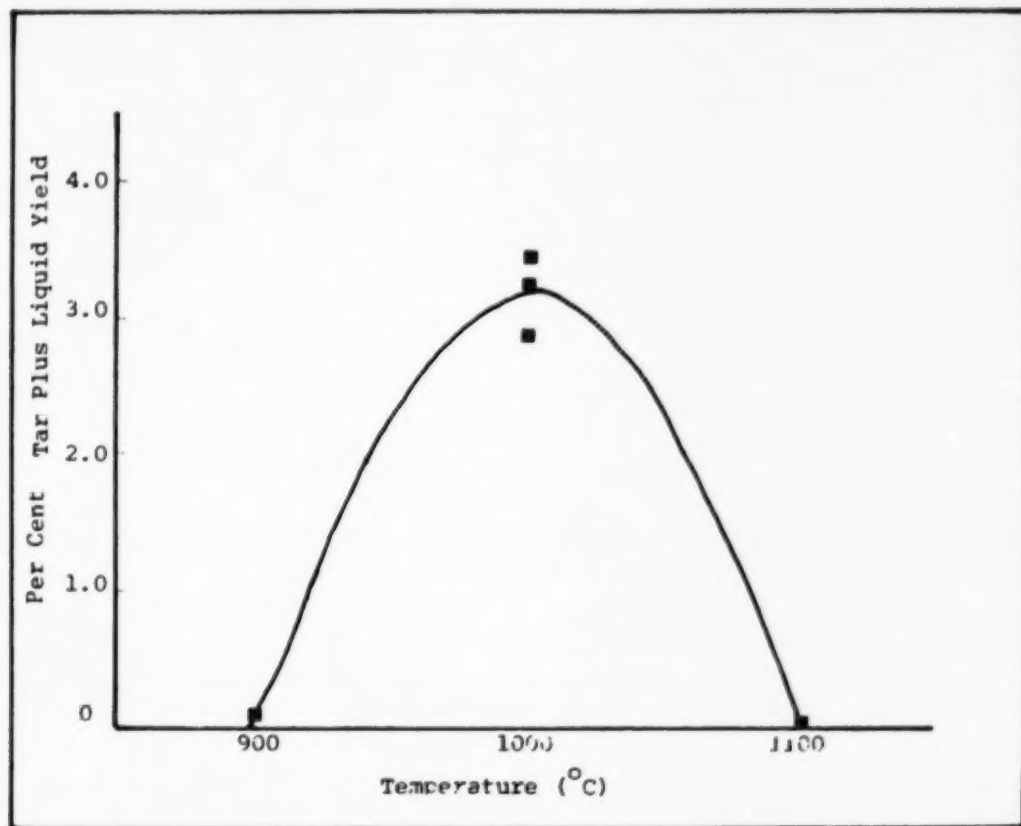


Figure 4.3 Effect of Temperature on tar and liquid yield,
Residence Time 30 s

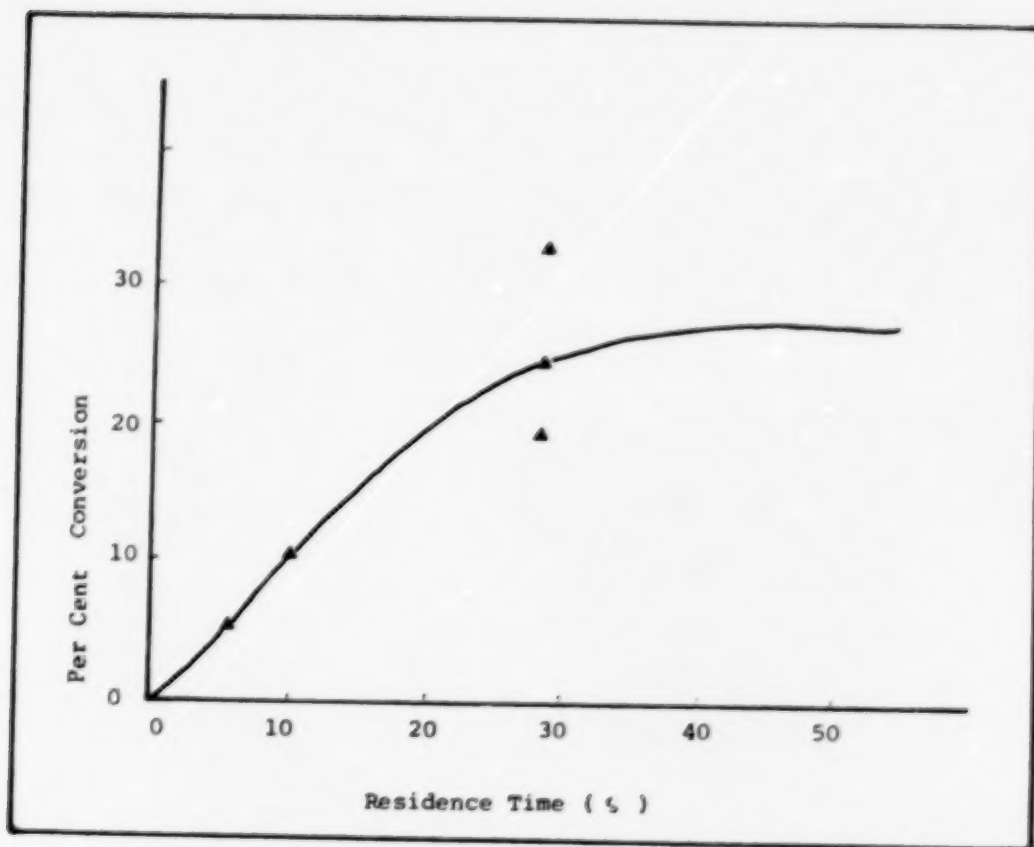


Figure 4.4 Effect of Residence Time on Conversion,
Temperature 1000 °C

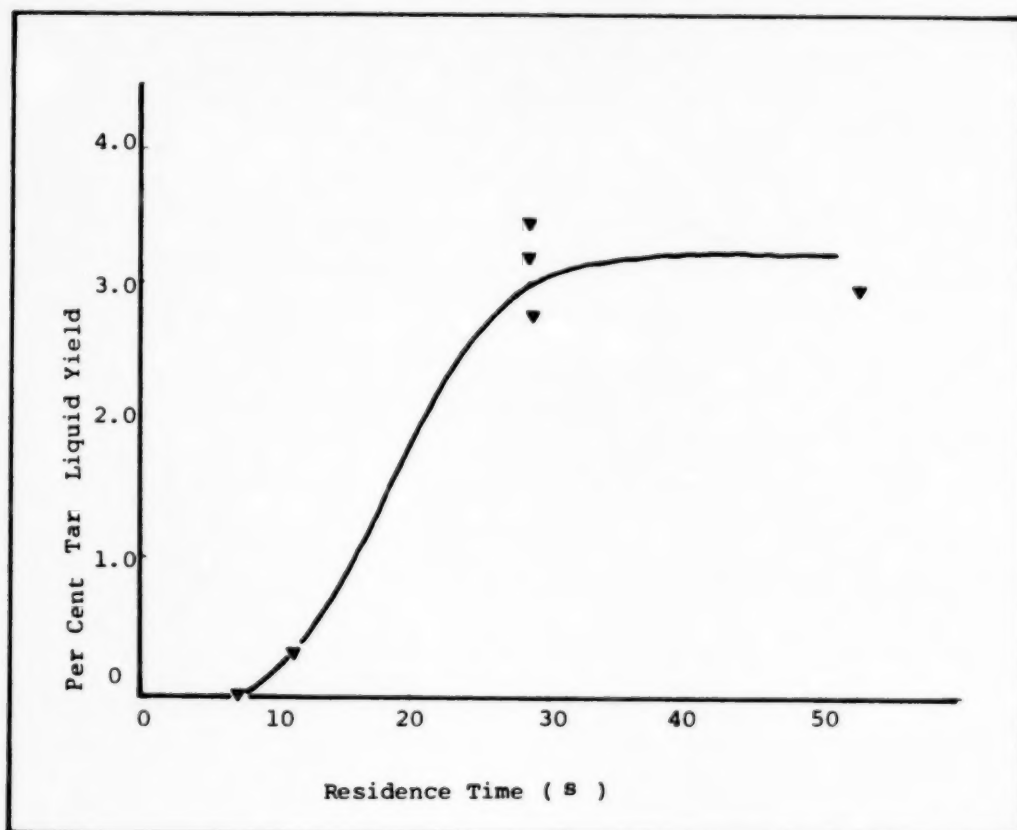


Figure 4.5 Effect of Residence Time on tar and liquid yield,
Temperature 1000°C, Pressure 1 atm

zones and an isothermal reaction zone which is significantly longer than the end zones (to minimize importance of end zone) must be present. The temperature-time history of the gas in the alumina reactor used in this study is not known, however, Fig. 4.6 shows the temperature distributions are quite peaked and the shape and position of the peak temperatures were found to depend on the flowrate and the temperature level. Because of the smaller surface to cross-section ratio in the 5 cm ID tube, it is reasonable to assume that the gas temperature is lower in this tube than in the mullite tube. A comparison of yields from two flow studies on methane pyrolysis can therefore at best be qualitative.

Second, the carbon formed during each experiment was not burned out of the tube. Since it was shown that the decomposition of methane is greatly accelerated in the presence of a surface deposit of carbon, this may be another reason the overall yields of liquids are lower in these preliminary experiments⁽¹⁾.

Considering the results obtained in this study the following recommendations are made:

1. Yields of pyrolysis liquids and tars depend strongly on reaction conditions. It is therefore recommended that every effort be made to minimize temperature gradients both axially and radially in the reactor by:
 - a) Choosing a small diameter tube so that the ratio of heating surface/cross-sectional area is high to promote rapid heat-up and isothermal conditions.
 - b) Choosing a minimal reaction tube wall thickness to reduce radial temperature differences.
 - c) Properly insulating the reactor ends to minimize heat losses and increase the length of the plateau (isothermal) region in the reactor.
2. Excessive carbon build-up inside the reactor been shown to reduce the yields of pyrolysis liquids. It is therefore recommended that the carbon be burned before each experiment. Furthermore, low CH_4 conversions as a result of short residence times will reduce the carbon build-up during an actual experiment.
3. Two points must be carefully considered:
 - a) the real temperature of the gas undergoing pyrolysis,

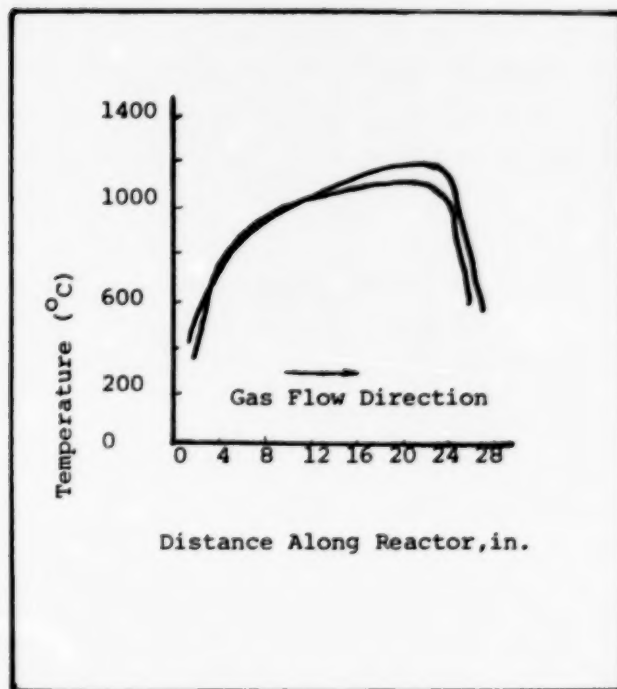


Figure 4.6 Temperature Profile inside reactor (35)

b) the time during which the gas is at this temperature.

Some effort must be made to heat the methane feed extremely quickly and to cool the products as quickly as possible in order to make the methane pyrolysis reaction occur only within the essentially isothermal reaction zone.

4. Any products formed at the high pyrolysis temperatures will be less stable than methane (except acetylene at 1500°C) and further reaction of these products will ensue unless they are quenched almost instantaneously.

4.4 Conclusion

Pyrolysis studies of methane in a tubular reactor have shown that liquid yields and yield of gaseous unsaturates are low in the temperature range 900-1100°C. Studies at higher temperatures in the same experimental set-up are prohibited by carbon plugging in the exit lines.

5. SUMMARY

A brief review of the existing indirect (e.g. Fischer-Tropsch and Mobil Oil) and direct processes for the conversion of natural gas to liquids has been presented. The indirect routes suffer from the high initial capital investment required and low overall thermal efficiency. The direct routes have so far given low liquid yields. There is indeed scope to design a catalyst which will decrease the reaction temperature, increase the conversion and promote the formation of desired liquid products.

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APPENDIX A

```

10 REM
30 REM Program calculates free energy of formation of hydrocarbons
40 REM
50 REM heat capacity of hydrocarbon gases expressed in the form
60 REM  $A + B T + C T^{**2} + D T^{**3}$ 
70 REM
80 REM heat capacity of hydrogen expressed in the form
90 REM  $A + B T$ 
95 IF N$='**' GO TO 150
100 REM
110 REM heat capacity of carbon (Graphite) expressed in the form
120 REM  $A + B T + C / T^{**2} + D / T^{**3}$ 
130 REM
140 REM
150 READ R
160 DATA 1.987
170 READ C1,C2,C3,C4
180 DATA 5.32692,3.6954E-04,-7.35084E05,1.2954E08
190 READ H1,H2
200 DATA 6.62,8.1E-04
210 OPEN 'SY1:HEAT.DAT' FOR INPUT AS FILE #5
220 OPEN 'LP:' FOR OUTPUT AS FILE #6
240 INPUT #5,N$
245 IF N$='**' GO TO 9999
250 INPUT #5,P,H,C
260 INPUT #5,P1,P2,P3,P4
265 INPUT #5,H0,G0
280 PRINT #6,N$
290 PRINT #6,P1,P2,P3,P4
300 PRINT #6
310 PRINT #6,' T -LN K K DEL G'
320 REM
330 REM
340 REM
350 REM calculating the integration constants
360 REM
370 LET T2=298^2
380 LET T3=T2*298
390 LET L=LOG(298)
400 I1=P1*298+P2*T2/2+P3*T3/3+P4*T2*T2/4
410 I2=H1*298+H2*T2/2
420 I3=C1*298+C2*T2/2-C3/298-C4/2/T2
430 I4=-H0/298
440 I4=I4+P*(P1*L+P2*298/2+P3*T2/6+P4*T3/12+I1/298)
450 I4=I4-H*(H1*L+H2*298/2+I2/298)
460 I4=I4-C*(C1*L+C2*298/2+C3/T2/2+C4/T3/6+I3/298)
470 REM
480 REM
490 T=300
500 REM
510 REM
550 REM calculating the equilibrium constant
560 L1=LOG(T)
570 T5=T*T
580 T6=T5*T
590 T7=T/2
600 K1=-H0/T
610 K1=K1+P*(P1*L1+P2*T7+P3*T5/6+P4*T6/12+I1/T)
620 K1=K1-H*(H1*L1+H2*T7+I2/T)

```

```
660 REM calculating the equilibrium constant
670 REM
680 K=EXP(K1/R-G0/R/298)
685 K2=-LOG(K)
690 REM
700 REM calculating the free energy of reaction
710 G=R*T*K2
720 IF T>2500 THEN GO TO 9998
730 PRINT #6,T,K2,H,G
740 T=T+100
750 GO TO 560
760 REM
770 REM
780 REM
790 REM
9998 GO TO 240
9999 END
```

